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ADHESIVES FOR DILUTE AND CONCENTRATED CRYOLITE SPRAYS USED IN WHITE-FRINGED BEETLE CONTROL OPERATIONS

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Cryolite was first used in field operations against white-fringed beetles (Graphognathus spp.) in 1939. Its use made possible control activities on every known type of infested property, as this insecticide is less injurious than calcium arsenate to leguminous plants and to livestock. The cryolite was first applied as a dust, but difficulty was encountered in keeping an adequate coverage on the plant foliage because of the frequent rains during the adult emergence season in the Gulf coast area where the beetles were found. Various dust adhesives were tested by the Division of Cereal and Forage Insect Investigations, but none were found effective. A definite need therefore existed for a cryolite formulation with adhesive quality which would assure effective coverage for a much longer period than that afforded by dusts.

In 1940 dilute cryolite sprays with fish oil as the adhesive agent were first used against white-fringed beetles. These sprays were capable of maintaining adequate residues after several inches of rainfall, and their use was extended to all control areas as quickly as equipment could be provided. Unfortunately, dilute sprays require the application of approximately 175 gallons of spray liquid per acre, which necessitates heavy equipment and limits their use on cultivated crops. Dust was still the only practicable means for controlling white-fringed beetles in cultivated fields.

Because of the limited usefulness of dilute sprays in the over-all control program, experiments with concentrated sprays were initiated in Gulfport, Miss., in 1940 by S. F. Potts, of the Division of Forest Insect Investigations, while on temporary loan to the Division of Cereal and Forage Insect Investigations. Two small power atomizers and hand atomizing apparatus were used for applying the sprays. Cryolite (and calcium arsenate) applied as concentrated sprays manifested heavier initial deposits, better adherence to the foliage, and greater effectiveness in reducing adult beetle populations than when applied as dilute sprays. Only 5 gallons of finely atomized concentrated spray appeared to give an adequate coverage, whereas 200 gallons of dilute spray was necessary.

1/ The writers acknowledge the assistance of L.E. Smith (resigned) in the dilute-spray studies, R. Q. Gardenhire (resigned) in the field tests, and William Breland in the chemical laboratory.

During the fall of 1940 and the spring of 1941, a concentrated-spray machine suitable for regular control operations was developed. This consisted essentially of a blower delivering a blast of air through a 4-inch nozzle provided with small jets, through which a constant flow of spray material was pumped. Later the jets were superseded by a conventional potato-spray nozzle, which reduced clogging and was less expensive. It was not until 1943, however, that the concentrated-spray machine was tested extensively in the field. In the meantime a definite need existed for a dilute-spray formula with an adhesive agent other than fish oil. This material was becoming increasingly difficult to obtain during the war years, was comparatively expensive, and was objectionable for urban use because of its odor. A series of tests to find a satisfactory substitute for fish oil in dilute cryolite sprays was therefore initiated.

Dilute-Spray Studies

Laboratory Tests.--A special turntable machine (fig. 1) was devised whereby experimental amounts of each spray formulation could be applied to waxed glass plates or to plants mounted on the turntable and then subjected to different amounts of artificial rainfall. By this method it was possible to select in a comparatively short time those sprays which appeared most promising from the large number tested.

The waxed plates were prepared by dipping glass slides into a saturated solution of beeswax in carbon tetrachloride and allowing them to dry. The spray was applied with a specially constructed machine holding 2 gallons of spray liquid, and the pressure was kept constant in all tests with the necessary pressure gages. Eighteen plates were treated with each test spray during 15 revolutions of the turntable. The plates were allowed to dry for 24 hours, and six were then selected at random for determining initial deposits. Six other plates were subjected to 3 inches of artificial rainfall, and the remainder to 6 inches. The cryolite deposits and residues were determined chemically by scraping the wax and cryolite from the treated surfaces into a Claisen flask and quantitatively analyzing the contents for cryolite, using the Willard and Winter method for fluorine determination.[2]

The adhesives tested, together with the amounts that would be included with 12 pounds of synthetic cryolite (88% sodium fluoaluminate) in 100 gallons of total spray liquid, were as follows:

Aluminum sulfate 3 lb., lime 1 lb.
Ferrous sulfate 2 lb., lime $\frac{1}{2}$ lb.
Zinc sulfate $3\frac{1}{2}$ lb., lime $1\frac{1}{2}$ lb.
CM-705 (a byproduct in manufacture of linseed oil) 3 lb.
Washed linseed oil 6 lb.
Washed linseed oil 6 lb., soda ash 0.15 lb.
Ammonium caseinate 3 lb.

2/ Willard, H. H., and Winter, O. B. Volumetric method for determination of fluorine. Indus. and Engin. Chem., Analyt. Ed. 5: 7-10. 1933.

Ammonium resinate $\frac{1}{2}$ lb.
Cottonseed oil 3 lb.
Keltex (sodium alginate product) 1 lb.
Kelgin (sodium alginate product) $\frac{1}{2}$ lb.
Spraysoy (soybean product for agricultural sprays) 3 lb.
Superloid (soybean product for agricultural sprays) $\frac{1}{2}$ lb.

When more than one ingredient is listed above (with the exception of washed linseed oil and soda ash), the two chemicals combine in the spray tank, forming a freshly precipitated hydroxide gel, and the amounts given are based on the stoichiometric combining weights. Soda ash was added to the washed linseed oil in order that it might react with the excess acid present in this product and thus prevent flocculation of the cryolite. In each series of tests fish oil was used as an arbitrary standard at the rate of 3 pounds per 100 gallons of spray.

The following formulations proved most satisfactory from the standpoint of adhesiveness, cost, and availability of ingredients: CM-705, aluminum sulfate and lime, ferrous sulfate and lime, and zinc sulfate and lime. Since the aluminum hydroxide gel formed by the reaction of aluminum sulfate and lime proved to be so satisfactory, other salts, such as sodium carbonate and magnesium carbonate, were tested with aluminum sulfate in the proper stoichiometric amounts to determine whether or not the gels thus formed would have physical qualities conducive to better adhesiveness in sprays. This was not found to be so.

Field Tests.--Several series of field tests were then conducted in which each of the promising spray formulations was applied to a 1/10-acre test plot with a small dilute-spray machine. In each series of tests gallberry (*Ilex glabra* L.) foliage was collected from the field and chemically analyzed to determine initial cryolite deposits. From one to three additional samplings were made thereafter, depending upon the amount of rainfall and other weather conditions. After the third series of tests the zinc sulfate-lime spray was eliminated as being less satisfactory than the other three formulations. The adhesiveness of the three remaining sprays is shown in table 1. Results with fish oil are also included for comparative purposes.

On the basis of the mean results, CM-705 was the best adhesive, followed by aluminum sulfate-lime, fish oil, and ferrous sulfate-lime. CM-705 was too expensive to justify its use in preference to the aluminum sulfate-lime combination, since it was only slightly superior in retaining cryolite residues. Moreover, when the median was considered as the statistical criterion, the aluminum sulfate-lime formulation was better than any of the other three sprays, and the results were more consistent than those obtained with CM-705. It was therefore decided to test the cryolite-aluminum sulfate-lime dilute spray in regular control operations.

Table 1.--Loss from initial deposit of dilute cryolite spray containing various adhesives, Gulfport, Miss., June, July, and August 1944.

Test	Rain	CM-705	Ferrous sulfate and lime	Aluminum sulfate and lime	Fish oil
	Inches	Percent	Percent	Percent	Percent
1	1/	--	57	57	60
2	0.94	19	--	40	61
3	1.34	41	64	62	78
4	.23	13	26	41	50
5	2.29	75	98	82	84
6	.44	52	57	46	45
7	.44	61	68	51	43
8	1.18	82	85	75	77
9	.74	61	79	61	68
10	.92	80	88	73	81
Mean		54	69	59	65
Median		63	70	59	65

1/ No record.

Control Demonstrations.--Field control demonstrations were conducted in the Gulfport and Hattiesburg areas with regular dilute-spray machines (fig. 2). In the Gulfport area tests were conducted in two fields. Half of each field was treated with cryolite spray containing fish oil as the adhesive agent, and the other half with cryolite spray containing aluminum sulfate-lime. In each field the aluminum sulfate-lime combination gave higher adult-beetle mortalities. When the results of these two tests were combined, 76 percent mortality was obtained with the fish-oil spray and 86 percent with the aluminum sulfate-lime formulation. In the Hattiesburg area tests were conducted on only one field, and a higher mortality was also obtained with the cryolite spray containing the aluminum sulfate-lime adhesive.

Concentrated-Spray Studies

In 1943 large-scale field tests were conducted with the concentrated-spray machine developed by the Division of Domestic Plant Quarantines (fig. 3). This machine proved to be highly satisfactory for securing adequate adult-beetle mortalities at a cost much below that of dilute sprays or dusts. The formulation then used was as follows: Cryolite 50 pounds, 40-percent Aresket (sodium monosulfonate of monobutyldiphenyl) 1 quart, raw linseed oil 5 quarts, and water 18 gallons. Aresket was subsequently superseded by Daxad 11 (sodium salt of

polymerized alkylaryl sulfonic acids) and Daxad 14 (sodium salt of polymerized alkylaryl sulfonic acids and an inorganic suspending agent), as the latter products are both suspending and wetting agents and minimize settling of the mixture in the concentrated-spray tank.

Because linseed oil was unavailable at that time, a series of experiments was initiated to develop a concentrated spray with ingredients comparatively inexpensive and available during the war years. It was desirable that the spray mixture should be (1) highly fluid, (2) readily suspended with a minimum of agitation, (3) sufficiently adhesive to withstand the heavy rainfall characteristic of this area, (4) easily prepared, and (5) as inexpensive as possible. Fish oil was undesirable from an over-all standpoint, because of its offensive odor. Furthermore, this adhesive in concentrated sprays required expensive wetting and suspending agents, which increased the difficulty of preparation and the cost of the final spray mixture.

Laboratory Tests.--Since the aluminum hydroxide gel formed by the reaction of lime with aluminum sulfate was shown to be as adhesive as fish oil in dilute cryolite spray mixtures, it was believed that this gel might also constitute a satisfactory adhesive in concentrated sprays. Therefore, a large number of laboratory tests were conducted on the turntable apparatus with aluminum sulfate in amounts ranging from $2\frac{1}{2}$ to $4\frac{1}{2}$ pounds per 50 gallons of total spray, together with lime or sodium silicate (water glass) in the proper stoichiometric proportions, to determine which quantity would be most adhesive and still yield a relatively fluid spray. The concentrated spray contained 2 pounds of synthetic cryolite per gallon of total spray liquid. The sprays were applied with the concentrated-spray machine (as shown in fig. 3) to freshly picked gallberry foliage placed in small flasks of water and mounted on the revolving turntable. At first the waxed plates were used, but it was soon found that electrostatic charges made the comparatively heavy deposit of cryolite from the concentrated-spray machine adhere to the waxed surfaces when subjected to artificial rainfall whether or not an adhesive was included. Therefore, the foliage was substituted for the waxed plates. After the spray residue on the foliage had been allowed to dry for 24 hours, a sample consisting of one-third of the foliage was taken at random for determining the initial cryolite deposit, and the remaining thirds were subjected to 2 and 4 inches, respectively, of artificial rainfall applied with a specially constructed apparatus. These leaves were then chemically analyzed for cryolite residues.

A large number of laboratory tests conducted in this manner indicated that a concentrated spray consisting of synthetic cryolite 100 pounds, aluminum sulfate 3 pounds, sodium silicate 9 pounds, and water to make 50 gallons was very fluid, easy to resuspend after hours of settling, and more adhesive than the fish oil spray under the conditions of these experiments.

Field Tests.--When tested in the field the synthetic cryolite-aluminum sulfate-sodium silicate spray was found to be totally unsatisfactory. Upon exposure to natural weathering the gels (aluminum hydroxide and silicic acid) formed by the reaction of aluminum sulfate

and sodium silicate became granular upon desiccation, and the spray deposit was easily removed by wind, mechanical shock, and especially rain. This was found to be true also for the aluminum sulfate-lime concentrated-spray formulations.

A nondrying mineral oil was added to the aluminum sulfate-sodium silicate spray to determine whether or not it would delay granulation. Several different oils were tested, and Straw Oil-340, a medium summer oil, was found to be the most satisfactory as well as the least expensive. Although this oil was ineffectual in the aluminum sulfate-water glass spray with synthetic cryolite, it did increase the adhesiveness with natural conditioned cryolite. The natural cryolite used in 1945 contained 0.25 percent of conditioning agent added by the manufacturer. When this product was used in concentrated sprays, Igepal (a condensation product of ethylene oxide and an alkylated cresol) was added as a wetting agent.

Because of the low unsulfonatable residue (80 percent) of Straw Oil-340, it was believed that considerable damage might result from its use on crop foliage during the summer season. Therefore, foliage-injury tests were initiated at the Alabama State Prison Farm at Atmore. The conditioned natural cryolite-Igepal-aluminum sulfate-water glass-Straw Oil spray and the synthetic cryolite-Daxads 11 and 14-fish oil spray were applied to the following crops at the rate of 6 gallons (1 quart of Straw Oil or fish oil) per acre, with the concentrated-spray machine: Carrots, beets, tomatoes, cotton, black-eyed peas, crowder peas, lima beans (small and large), and corn (5 to 6 feet tall). No burning of the foliage resulted, even though the sprays were applied at an air temperature of 90° F. and the weather was very hot during the week between treatments and observations. No injury was noticed even in spots where an extremely heavy deposit was applied, as at the beginning of a row. It therefore appeared that Straw Oil-340 was reasonably safe for use on most crops from a foliage-burn standpoint. The conditioned natural cryolite-aluminum sulfate-water glass-Igepal-Straw Oil spray was later used in several control areas without any subsequent plant injury. This included the frequent spraying of ornamentals in Amite and New Orleans, La.

Although this spray mixture was used in several areas with complete satisfaction, studies were continued for improving the formulation. It was found that the aluminum sulfate and water glass could be deleted from the spray mixture, and the new formulation—i.e., conditioned natural cryolite, Igepal, and Straw Oil-340—was even more adhesive than the one including these two ingredients. This new spray was also extremely fluid and did not settle out in the spray tank even when left for several days with no agitation. It was also more adhesive and easier to prepare than the synthetic cryolite-Daxads-fish oil mixture, and the least expensive of all the spray formulations tested. Furthermore, because of its nonoffensive odor, this spray could be used in many places where fish oil would be objectionable.

A large-scale field test was conducted at Gulfport, Miss., to compare the most promising spray mixtures selected from the preliminary

testings of 37 spray combinations. Test plots $\frac{1}{2}$-acre in size were sprayed with the different formulations on three occasions. Chemical analyses of gallberry foliage growing naturally on these idle-land plots were made just prior to each treatment, immediately thereafter, and after each rainfall of at least $\frac{1}{2}$ inch. If there was less than $\frac{1}{2}$ inch of rainfall for 8 days, samples were collected for that period to determine the effect of this type of weathering on the different spray deposits. In all tests 2 pounds of cryolite, natural or synthetic, was contained in each gallon of total spray. These spray mixtures were prepared by running approximately 35 gallons of water into the 50-gallon spray tank and, with the agitator operating at full speed, adding the other ingredients, and finally sufficient water to make 50 gallons of total spray. The results are shown in table 2.

The total precipitation was 4.27 inches during this test. Immediately afterward there was a rainfall of 5.42 inches spread over a 9-day period, with 4 inches falling in a single day. A further sampling was then made from the test plots treated with the three best spray formulations as listed in table 2, and the analyses showed the following reductions in deposits: No. 1, 47 percent; No. 2, 70 percent; and No. 3, 84 percent. It is therefore evident that the natural cryolite-Straw Oil formulation (No. 2) was better than the synthetic cryolite-fish oil spray (No. 3) even under excessively heavy rainfall. This spray is about 10 percent less expensive than the fish oil spray, and when cost of the adhesive materials alone is considered, a saving of approximately 70 percent is possible. As noted from table 2, Straw Oil cannot be substituted for fish oil in the Daxad-synthetic cryolite spray, as the resultant mixture is not sufficiently adhesive. Daxads must be included, even in Straw Oil sprays, with synthetic cryolite, as previous tests have shown that their exclusion resulted in a mixture which settled badly in the spray tank.

Spray No. 1 was the most adhesive formulation tested. Although this spray is comparatively expensive, it may be applied much less frequently in areas having excessive rainfall, where it would remain effective for long periods when spray equipment could not be operated in the field. Aluminum sulfate and water glass cannot be omitted from this formulation, as they form an electrolyte which prevents inversion of the spray mixture. This electrolyte may be omitted when unconditioned natural cryolite is used or when Straw Oil-340 is used instead of fish oil.

In 1942 a special study was made to determine the relationship between cryolite residues on foliage and adult beetle mortalities in potted-plant cage tests. The mortalities were determined by the Division of Cereal and Forage Insect Investigations and the chemical analyses by the Division of Domestic Plant Quarantines. Since cotton leaves were used for those studies and gallberry foliage in the tests previously reported, an attempt was made to interpolate the mortality-residue ratios obtained in the 1942 tests with the residues from the various concentrated sprays on gallberry foliage. Cotton, peanut, and gallberry leaves were photographed and the leaf images cut out and weighed, to

Table 2.--Adhesiveness of various cryolite concentrated-spray formulations. Gulfport, Miss., August-September 1945.

No.	Formulation (Quantities per 50 gal. of spray)	Cost	Loss from initial deposit 1/	Cryolite remaining 2/
			Percent	Milligrams
1	Aluminum sulfate 4 lb. Water glass 12 lb. Igepal 1 pt. Natural cryolite 3/ 100 lb.	$12.26	38	118
2	Igepal 1 pt. Natural cryolite 3/ 100 lb. Straw Oil-340 2 gal. Kerosene 4/ up to 1 pt.	10.85	54	55
3	Daxad 11 4 oz. Daxad 14 28 oz. Synthetic cryolite 100 lb. Fish oil 2 gal.	12.14	60	45
4	Aluminum sulfate 4 lb. Water glass 12 lb. Igepal 1 pt. Natural cryolite 3/ 100 lb. Straw Oil-340 2 gal.	11.17	72	35
5	Daxad 11 4 oz. Daxad 14 28 oz. Synthetic cryolite 100 lb. Straw Oil-340 2 gal.	11.05	75	30
6	Aluminum sulfate 4 lb. Water glass 12 lb. Igepal 1 pt. Natural cryolite 3/ 100 lb.	10.90	80	25
7	Igepal 1 pt. Natural cryolite 3/ 100 lb. Kerosene 4/ up to 1 pt.	10.58	83	26

1/ Average of 8 collections.

2/ Per 12 grams (dry weight) of gallberry foliage. Average of 9 collections.

3/ All natural cryolite contained 0.25 percent of conditioner added by the manufacturer.

4/ Before final addition of water to reduce foaming.

obtain the comparative dry weight-leaf surface ratios in the three plants. When cryolite residues on gallberry foliage after 4.27 inches of rainfall are considered, only the first three formulations of the 1945 tests as listed in table 2 should give the highest mortality reported in the 1942 tests, viz., 92.8 percent with natural cryolite.

Field tests were conducted at Florala, Ala., in which adult-beetle mortalities were used as the criterion of effectiveness of the different spray formulations. The sprays were applied to vegetation in idle and cultivated fields at the rate of 2 pounds of cryolite per gallon of spray with the concentrated-spray machine delivering at the rate of 6½ gallons per acre. The natural cryolite-Igepal-Straw Oil formulation (No. 2) was compared with the synthetic cryolite-Daxads sprays (Nos. 3 and 5). Also included in these tests was a spray formulation containing natural cryolite with aluminum sulfate and water glass. This was an opportunity to study the effect of aluminum sulfate on cryolite sprays. It was believed that the inclusion of aluminum sulfate might break down the cryolite and render it ineffectual as an insecticide. The results of these tests are shown in table 3.

Table 3.--Mortality of white-fringed beetles after spraying with various cryolite concentrated-spray formulations and after dusting with natural and synthetic cryolite. Florala, Ala., 1945.

Formulation No.	3rd day (rain 1.5 in.)	7th day (rain 3.6 in.)	14th day (rain 5.1 in.)	Average
	Percent	Percent	Percent	Percent
2	84	76	50	70
3	83	73	42	66
4	85	71	26	61
5	69	40	22	44
Cryolite dusts:				
Natural, with conditioner	49	46	23	40
Synthetic	49	44	24	39

These mortality tests further substantiated the results obtained with chemical analyses, viz., that the natural cryolite-Straw Oil (No. 2) formulation was just as good as, or better than, the synthetic cryolite spray with fish oil (No. 3). Moreover, as previously determined by chemical analyses, the synthetic cryolite-Daxads spray with Straw Oil (No. 5) was inferior to that with fish oil (No. 4). The aluminum sulfate and water glass showed no detrimental effect on the toxicity of the cryolite

spray in which it was included (No. 2). The mortalities with conditioned natural cryolite dust were practically the same as those with synthetic cryolite. Evidently, the differences between these two materials were manifested only in the spray formulations tested. The apparent decreasing mortalities in table 3 are due to the counting of beetles emerging before exposure to the insecticide, and to removal of dead beetles by ants.

Control Operations.—During the 1945 control season cryolite concentrated sprays with aluminum sulfate, lime (or water glass), and Straw Oil-340 were employed extensively in all white-fringed beetle control areas. These Straw Oil sprays were made only with conditioned natural cryolite, as tests had demonstrated their inefficacy with synthetic cryolite. The synthetic material was used as a dust, and in sprays with fish oil as the adhesive where the offensive odor was not a factor. Both sprays appeared to be equally satisfactory against adult white-fringed beetles. Towards the end of the season the aluminum sulfate-water glass combination was deleted from the conditioned natural cryolite-Igepal-Straw Oil formulation, and in actual control operations this new spray appeared to maintain better cryolite deposits than the synthetic cryolite-Daxads-fish oil spray. No foliage injury from Straw Oil-340 was reported, although 5,000 gallons of this material were used during the control season and some of the heavy dosages were applied to ornamentals.

An extremely concentrated spray — conditioned natural cryolite 250 pounds, Igepal 1½ pints, Straw Oil-340 6 gallons, and water to make 50 gallons — was applied by airplane in regular control operations during 1946. This spray, which contained 5 pounds of insecticide per gallon of total liquid, was applied at the rate of 2.8 gallons (14 pounds of cryolite) per acre with complete satisfaction. There was no agitator in the spray tank of the airplane, but none of the pipe lines were clogged during operations. This spray was so well suspended that no residue was left in the tank after the lines had been completely emptied. An experimental batch of this highly concentrated spray was left undisturbed in the spray tank for 7 months, but it was easily resuspended after that period with a small amount of agitation.

Summary and Conclusions

Studies on adhesive agents for dilute and concentrated cryolite sprays were conducted in 1944 and 1945 at Gulfport, Miss. Although the primary purpose was to find substitutes for linseed oil, which was unavailable, and fish oil, which was scarce and expensive during the war years, several formulations were developed which contained adhesive agents as satisfactory as fish oil and were also less expensive and odoriferous. The sprays were also more easily prepared. Aluminum sulfate and lime formed a satisfactory adhesive agent for natural or synthetic dilute sprays and Straw Oil-340 in conditioned natural cryolite concentrated sprays. A highly concentrated spray was developed and used successfully in airplane equipment. The formula was conditioned natural cryolite 250 pounds, Igepal 1½ pints, Straw Oil-340 6 gallons, and water to make 50 gallons.

It is evident from these tests that the turntable technique in adhesive studies in the laboratory was not satisfactory, especially when concentrated sprays were used. Artificial weathering, such as indoor drying for several hours, the use of an electric fan to simulate wind conditions, controlled rainfall from special machines, or any combination of these methods, could not be used in lieu of natural weathering for determining the comparative efficacy of different spray formulations. Moreover, artificial surfaces, as glass or wax-coated glass, were found to be less satisfactory than natural leaf surfaces for studying the adhesive qualities of different cryolite spray formulations.

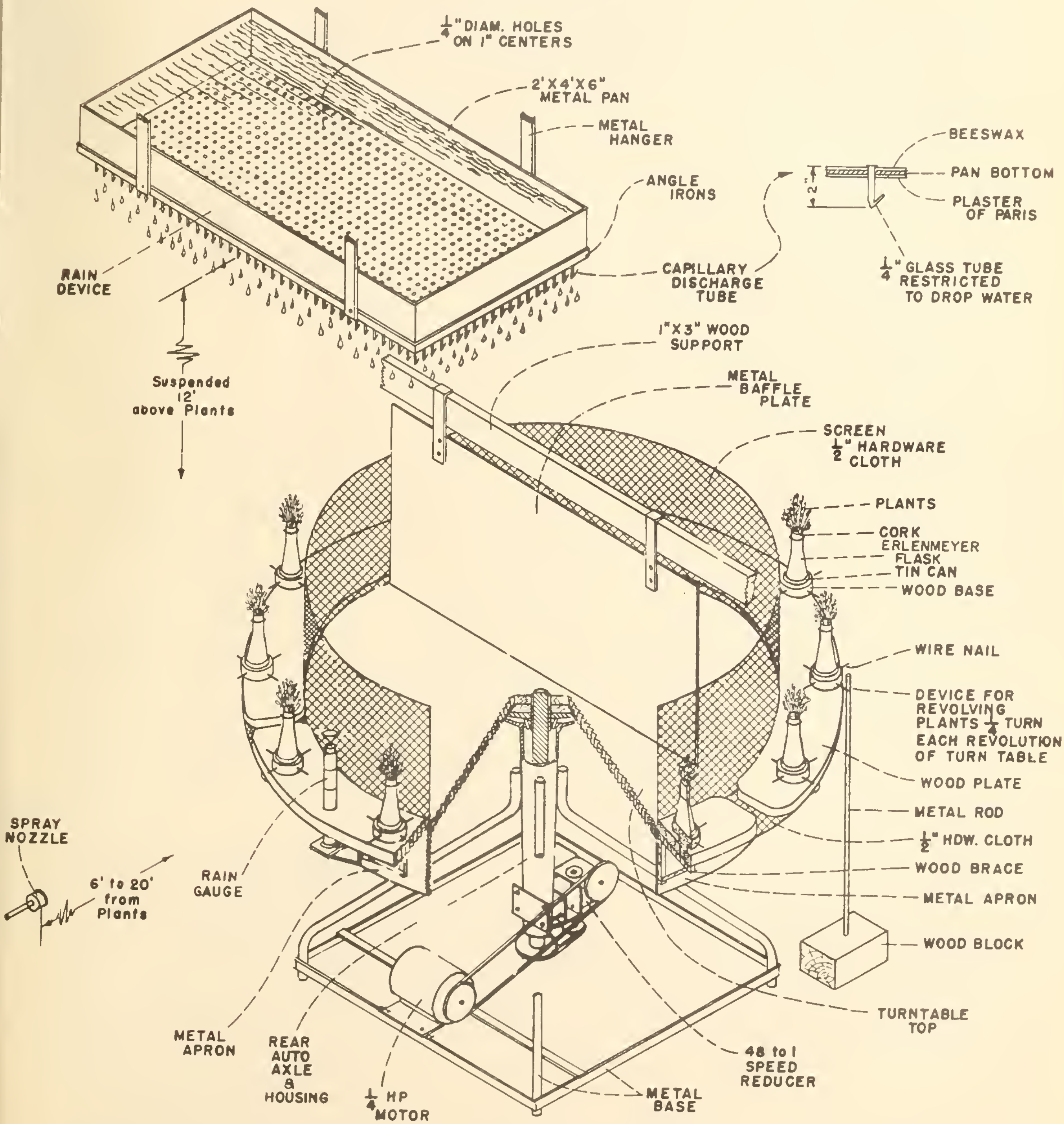

Figure 1.--Turntable apparatus for testing adhesiveness of cryolite sprays.

Figure 2.--Dilute-spray machine applying 150 to 200 gallons of cryolite spray per acre.

Figure 3.--Concentrated-spray machine applying 6 to $6\frac{1}{2}$ gallons of cryolite spray per acre.